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Rolling-induced microstructure change in $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ bulk metallic glass

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The microstructures and free-volume evolutions of as-cast and pre-annealed $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ bulk metallic glasses during rolling deformation have been investigated. No phase transformation is detected in the as-cast/rolled specimen. However, the structural stability of the glass against plastic deformation is worse after pre-annealing, indicated by nanocrystallization in pre-annealed/rolled specimens with large deformation degrees. Moreover, with increasing deformation degree, the free-volume content in a pre-annealed/rolled specimen increases at a lower average rate than that in an as-cast/rolled specimen.

metallic glass, free volume, plastic deformation, nanocrystallization

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Bulk metallic glasses (BMGs) have attracted much attention because of their properties such as high fatigue strength, high hardness, good castability, and excellent wear and corrosion resistances [1–8]. However, during compressive or tensile tests at temperatures far below the glass-transition temperature, failure of BMGs usually occurs along a single shear band without much macroscopic plasticity. Their low global plasticity and ductility limit their applications as engineering materials [9], and much attention has been focused on their deformation and fracture mechanisms. Spaepen showed that plastic deformation in a metallic glass is realized by a series of atomic diffusional jumps associated with free volume [10]. The introduction of free volume into shear bands leads to a local lowering of the viscosity, and, as a result, an abrupt break takes places along the shear band. Obviously, the mechanical properties of metallic glasses are closely related to the free-volume content.

Four methods can be used to change free-volume content: cooling the melt at different rates during solidification [11], annealing the metallic glass below the glass-transition temperature [12], reheating the metallic glass to above the glass-transition temperature and then cooling down quickly [13], and plastic deformation [14–17]. The principle behind these methods is that metallic glasses are thermodynamically metastable. Their structure can be changed from one state to another state by heating or mechanical deformation. Many studies have addressed the effects of plastic deformation on the free-volume content of metallic glasses [18–20], but very little attention has been paid to the dependence of free-volume evolution during deformation on the initial state of the glass. In this study, rolling deformation was performed on as-cast and pre-annealed $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ BMGs, and their free-volume content evolutions were investigated.

1 Experimental procedure

Alloy ingots of nominal composition $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ (atomic per cent) were prepared by arc melting a mixture of pure Zr (99.9%), Al (99.99%), Ni (99.99%), Cu (99.99%), and Ag (99.99%) under a Ti-gettered argon atmosphere. The ingots were inverted and remelted six times to ensure

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*Corresponding author (email: jfli@sjtu.edu.cn) compositional homogeneity, and then suction-cast into a water-cooled Cu mold to form 60-mm-long rectangular plates of thickness and width 1 mm and 10 mm, respectively. Some of the plates were annealed at 680 K (a temperature within the supercooled liquid region) for 9 min in a vacuum quartz tube, and then quickly cooled down to room temperature by moving the heating furnace away and watering the quartz tube. Both the as-cast and the pre-annealed plates were cut transversely into strips of width 3 mm. These strips were rolled at room temperature to different thicknesses in a twin-roller apparatus with a roller diameter of 100 mm. The deformation degree was denoted by the reduction in thickness, $\varepsilon=(h_0-h)/h_0$, where h_0 and h represent the specimen thickness before and after rolling, respectively. The strain rate was carefully controlled to be about 1×10^{-1} s^{-1} by narrowing the gap between the two rollers. The phase constitution of the specimen was examined using a Thermo ARL X-ray diffractometer (XRD) with monochromatic Cu Kα radiation. The microstructure was studied using a JEOL JEM-2100F high-resolution transmission electron microscope (HRTEM). The HRTEM foil was prepared by electrochemical twin-jet polishing in a solution of 5% perchloric acid and 95% ethanol at 243 K. The free-volume evolution was investigated using a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) under a flow of high-purity argon.

2 Results

2.1 Microstructure

The XRD patterns of as-cast and pre-annealed $Zr_{65}Al_{7.5}$-$Ni_{10}Cu_{12.5}Ag_5$ BMGs consist of only diffuse peaks (not shown here), indicating that they are amorphous in nature. Both types of BMG exhibit good ductility and are rolled up to a thickness reduction of 95% at a strain rate of 1×10^{-1} s^{-1}. DSC measurements demonstrate that the crystallization enthalpy of the as-cast/rolled specimen is about constant, independent of thickness reduction, whereas that of the pre-annealed/rolled specimen continuously decreases from 59.5 to 56.1 J g^{-1} as the thickness reduction increases from 0% to 95%; that is, pre-annealing worsens the structural stability.

Figure 1 shows the bright-field images of the specimens with a 95% thickness reduction. No contrast can be detected,

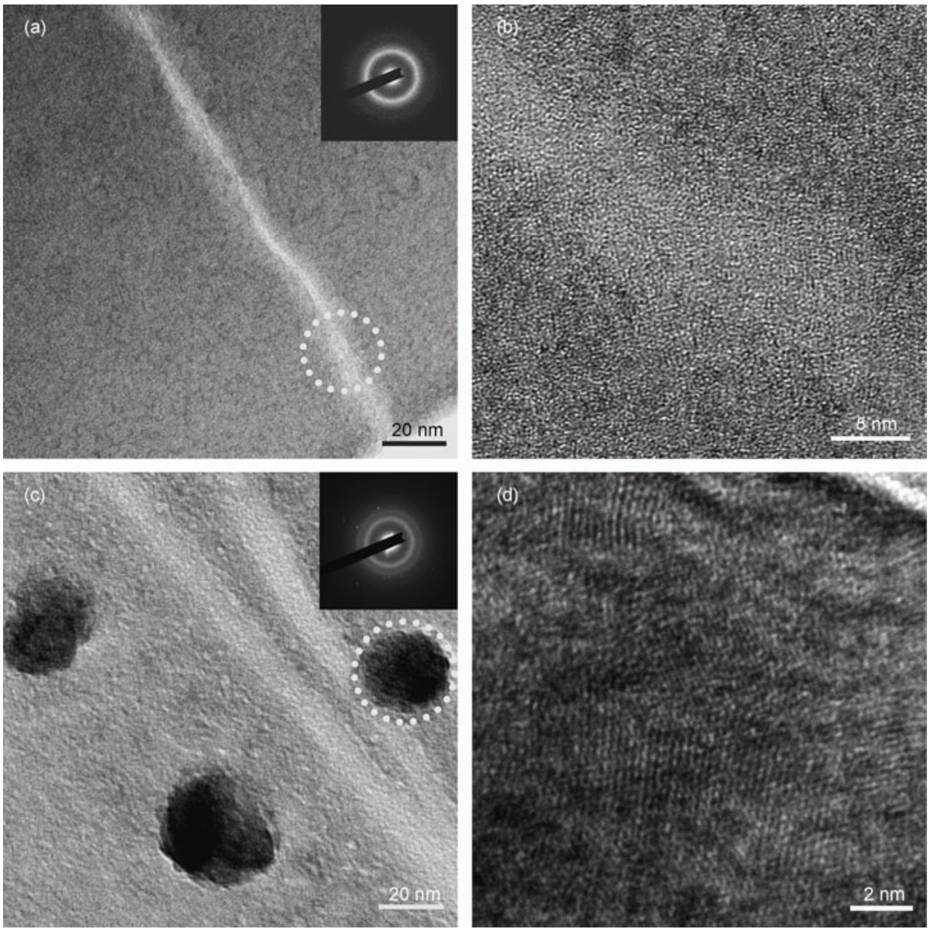

Figure 1 TEM bright-field images and SAED patterns of the as-cast (a) and pre-annealed (c) specimens rolled up to 95% thickness reduction. (b) and (d) are the HRTEM images of the selected regions in (a) and (c), respectively.

except for shear bands, in the as-cast/rolled specimen. The selected-area electron-diffraction (SAED) pattern taken from a 130-nm-diameter region containing the shear band consists of a broad diffraction halo and a faint larger halo; this is typical of an amorphous material (Figure 1(a)). At high magnification, no obvious lattice fringes can be observed inside or around the shear band, as shown in Figure 1(b), also implying that the as-cast/rolled specimen maintains the amorphous structure and no phase transformation takes place during the rolling. However, for the pre-annealed/rolled specimen rolled up to 95% reduction, some spherical dark precipitates with diameters of 20–30 nm can be found near or around the shear bands, and the corresponding SAED pattern contains some sharp diffraction spots (Figure 1(c)). The HRTEM images obtained from the precipitates show distinct lattice fringes (Figure 1(d)). Based on these results, we can conclude that the as-cast specimen exhibits excellent structural stability throughout the rolling process; however, the specimen subjected to annealing shows reduced structural stability and nanocrystallization occurs during the subsequent rolling deformation.

2.2 Free-volume evolution

Free volume in metallic glasses can be characterized by positron-annihilation spectroscopy (PAS) [14], density measurements [21], and differential scanning calorimetry (DSC) [22]. Here we use the DSC method developed by Beukel and Sietsma [23]. They proposed that the free-volume content in a metallic glass is proportional to the energy released during relaxation. Its variation can be characterized by the change in relaxation energy. Figure 2 shows the relative changes in the apparent specific heat ΔC_p below the crystallization temperature. The variation of the relaxation energy E_r with thickness reduction is shown in Figure 3. Because crystals do not contain so-called free volumes, their volume has been excluded in calculating E_r. It is obvious that pre-annealing reduces E_r, and it monotonically increases from 4.8 to 22.6 J g^{-1} for the as-cast/rolled specimen, and from 0.5 to 15.6 J g^{-1} for the pre-annealed/ rolled specimen, as the thickness reduction changes from 0% to 95%. Letting two sets of E_r values start to increase from zero though translational movement of the points, it can be clearly seen that the average rate of free-volume increase in the pre-annealed/rolled specimen is lower than that in the as-cast/rolled specimen.

3 Discussion

When the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ BMG was annealed at 680 K, solute segregation occurred, driven by the different heats of

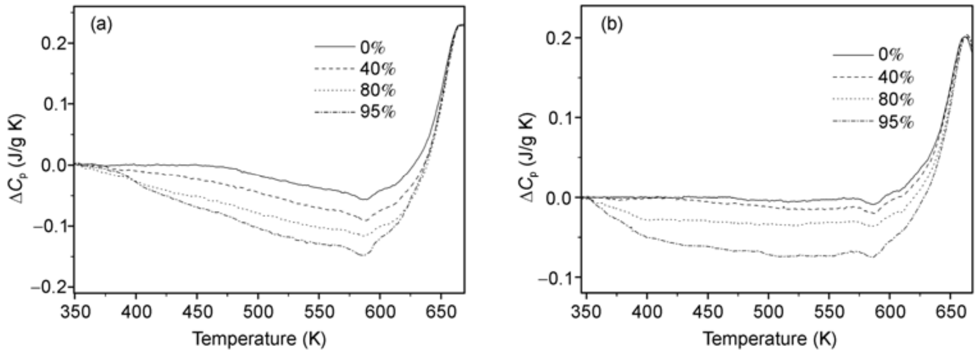

Figure 2 Comparison of specific heats of as-cast (a) and pre-annealed (b) specimens rolled with different thickness reductions.

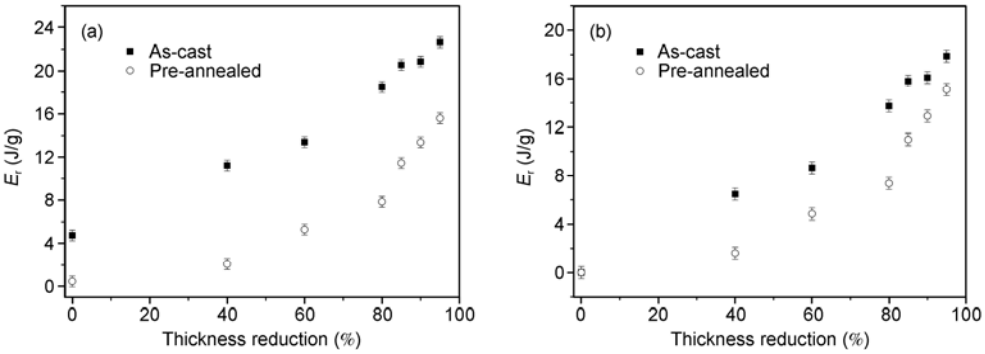

Figure 3 Variation of the relaxation enthalpy per unit mass (E_r) against thickness reduction: (a) without translational movement and (b) with translational movement.

mixing between the constituent elements. Solute diffusion over large distances is no longer needed if the glass is further crystallized. Thus, during rolling, some of the atoms in the segregation region near the shear bands are activated under the applied shear stress and transformed into the crystalline state. For the as-cast specimen, crystallization relies on long-distance diffusion of the solute, which is impossible during rolling. Therefore, the as-cast specimen exhibits better structural stability against rolling.

For a metallic glass subjected to plastic deformation, excess free-volume is created when an atom is squeezed into a smaller space under the applied stress. In the present work, the rolled metallic glass is composed of two parts: shear bands and the matrix. Obviously, the rolling-induced rise in the free-volume content mainly results from the formation of shear bands. The atoms in shear bands undergo violent flow, so the free-volume content in the shear bands is almost independent of the initial state of the glass. Thus, for the pre-annealed metallic glass, with less free volume, a larger increase in free-volume content should occur when it is deformed to the same degree. However, this prediction is inconsistent with the experimental results.

In general, a local region with abundant free volume facilitates nucleation and propagation of shear bands during plastic deformation. In this sense, the pre-annealed specimen containing less free-volume is unfavorable to the operation and formation of shear transformation zones (STZs), leading to a drop in the density of shear bands. On the other hand, nanocrystallization in the pre-annealed/rolled specimen upon severe rolling deformation results in crystal/glass interfaces in the alloy. At these interfaces, free volume is apt to annihilate [18]. As a result, the free-volume annihilation rate during plastic deformation increases. These two factors probably explain why the pre-annealed specimen subjected to rolling exhibits a smaller increase in free-volume content compared with that in the as-cast BMG.

4 Conclusions

The structural stability of $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ BMGs against inhomogeneous plastic deformation becomes worse after pre-annealing at 680 K for 9 min. When rolled at room temperature, nanocrystallization occurs in the pre-annealed/rolled specimen but not in the as-cast/rolled specimen. The average rate of increase in the free-volume content in the pre-annealed/rolled specimen is lower than that in the as-cast/rolled specimen. The initial free-volume content in the specimen, shear band density, and crystal/glass interface are probably the factors which influences the free-volume changes.

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